Structure-property relations of gold and graphene nanoporous actuators

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Chapter 2

Morphology and mechanical properties of metal and graphene nanofoams

The structure-property relations of gold and graphene nanoporous actuators do not only depend on the actuation mechanisms at the (sub)atomic scale, they are also influenced by the morphology of the nanoporous architecture. In this chapter we discuss in detail the different morphologies of gold and graphene nanofoams and to what extent the morphological parameters can be tuned to produce tailored architectures. Also, we discuss the mechanical properties of these materials.

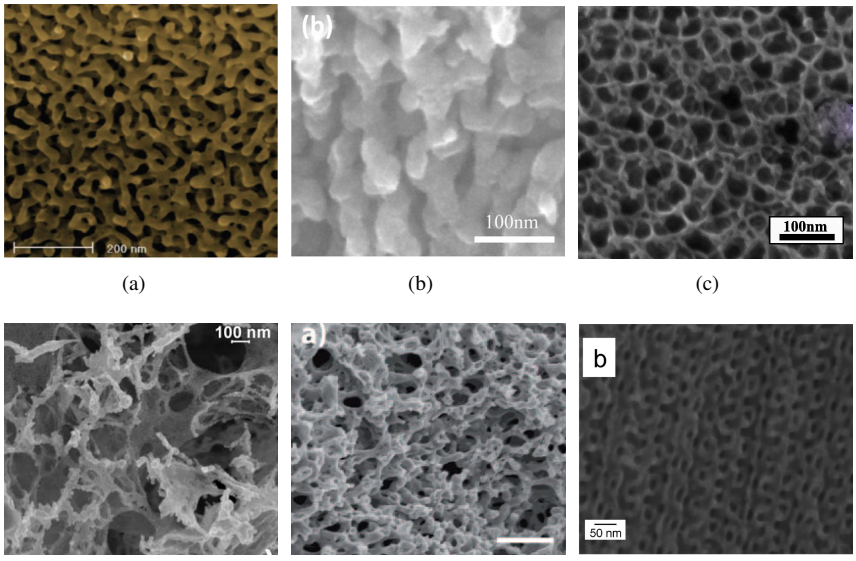
2.1 Morphology

2.1.1 Metal nanofoams

Two important physical aspects of nanoporous metals at small length scales are the size-dependent plastic strength and the influence of surface stress. In conventional materials science these features are seen as a consequence of processing at increasingly smaller dimensions. However, these features can also be exploited to design nanoporous actuators with optimal structural and actuation performance. Key in this approach is to utilize the morphological degrees of freedom offered by the cellular architecture which controls the internal surface area, mechanical stiffness and plastic strength of the nanofoams. Nanofoams having different morphologies are produced from copper, gold, nickel, palladium, platinum, silver and titanium [74, 76, 77, 90, 112–114] using several techniques such as dealloying, block-copolymer templating and combustion synthesis. Nanoporous gold (Fig. 2.1(a)) and nanoporous copper (Fig. 2.1(b)) prepared by dealloying have similar structures, while

nanoporous platinum produced by the same method slightly differs with mass agglomeration at the junctions, see Fig. 2.1(c). The architecture of nanoporous palladium and titanium, see Figs. 2.1(d)-2.1(e), prepared by combustion synthesis is different to that of the samples prepared by dealloying with a visible difference in ligament-connectivity. While the aforementioned samples have disordered architectures, nanoporous nickel shown in Fig. 2.1(f) has an ordered gyroidal structure. Nanoporous gold (NPG) is the most explored metal nanofoam and is generally prepared by chemical or electrochemical dealloying, a corrosion process in which the less noble component of an alloy is selectively removed [115–118], resulting in a monolithic bi-continuous structure consisting of connected solid ligaments and empty space forming separate interconnected networks, interpenetrating at a characteristic length scale of a few to tens of nanometers. NPG is prepared from silver-gold (Ag-Au) alloys with the Ag content in a larger proportion. Ligament diameters can easily be fine-tuned between 2 nm to 10 μm without changing the relative density or morphology (connectivity, ligament shape, pore shape) of the material [119–121]. Generally, NPG prepared by dealloying is available in polycrystalline form where the grain structure is retained from its alloy precursor [117, 120, 122]. Recently, however, also NPG prepared from a single crystalline alloy precursor has been reported [123].

The mechanical properties of NPG depend on the relative density, specific surface area and morphology. These can be tailored during fabrication by adjusting the composition of the precursor alloys and dealloying conditions or after fabrication by structural coarsening using thermal and acid treatments [101, 120, 124–129]. Generally, the relative density of NPG is determined by the weight fraction of Au in the Au-Ag alloy. It is reported that NPG samples also undergo an additional volume contraction of up to 30% during dealloying [130], further increasing the relative density compared to that determined from the weight fraction [112]. An experimental study on an alloy with a ternary composition $Au_5Pd_{20}Ag_{75}$ has revealed a novel NPG architecture with a dual microscopic length scale [90]. The resultant NPG has stacked nanoporous gold layers with a thickness in the submicrometer range which can be tailored by the grain size of the alloy precursor. The two-length-scale structure enhances the actuation properties of NPG, leading to charge-induced strains up to 6%, which are roughly 2 orders of magnitude larger than in NPG with the standard one length scale porous morphology. Next to the alloy composition, also the ligament and pore dimensions can be tailored by tuning the dealloying potential. The ligament size is found to decrease linearly with increasing dealloying potential, leading to a decrease from 22 to 10 nm when the dealloying potential is increased from 0.8 to 1.3 V [129]. The aspect ratio of ligaments in



(a) (b) (c)

(d) (e) (f)

Figure 2.1: Different morphologies of metal nanofoams. (a) Nanoporous gold prepared by chemical dealloying of $Au_{25}Ag_{75}$ (at%) [31]. (b) Nanoporous copper prepared by electrochemical dealloying of amorphous copper silicide [75]. (c) Nanoporous platinum prepared by electrochemical dealloying of amorphous platinum silicide [112]. (d) Palladium nanofoam prepared by combustion synthesis [76]. (e) Titanium nanofoam prepared by combustion synthesis (scale bar is 500 nm) [76]. (f) Ordered nickel gyroids prepared by block copolymers templating [77].

NPG typically lies between 1 and 3 [124, 131]. X-ray nanotomography studies have shown that the topology of nanoporous gold is similar to that of other bicontinuous structures created by phase separation, despite the radically different method used to produce the structure [132]. Also theoretical approaches such as Monte Carlo lattice-gas models are able to generate phase-separated structures with morphologies that closely resemble those of NPG [133]. Generally, in dealloyed NPG 3 to 4 ligaments connect at each node [134]. Another method to tune the ligament/pore dimensions is thermal coarsening, a post-dealloying treatment. It is driven by the tendency of the surface to attain a minimal energy state, which involves surface diffusion of gold atoms [101]. Coarsening is accompanied by a decrease in the surface area, an increase in the characteristic feature size, a decrease in the number of ligaments per volume and dead ends within the bulk of the structure [135].

Metal nanofoams prepared by dealloying have disordered architectures with randomly

interconnected ligaments. NPG samples prepared by Rosner et al. [135] are found to have residual strain inhomogeneities and spherical voids with diameters ranging from 1-5 nm. Parida et al. [130] proposed that the formation of NPG during dealloying is accompanied by lattice defects. The number of defects in the sample are found to increase with increased dealloying potential. A disadvantage of disordered foams is that these architectures, with non uniform cross-sectional ligaments and poor ligament connectivity, have rather poor mechanical properties compared to regular, ordered structures. Recently, Ivana et al. [77] prepared ordered nickel nanofoams having a gyroid morphology using a block-copolymer template method, see Fig. 2.1(f). The samples are stable and retain the morphology of the template with relative densities around 50%.

2.1.2 Graphene nanofoams

Three-dimensional (3D) graphene architectures such as porous films, scaffolds and networks, optimally benefit from the stable, highly conducting and large surface area of single graphene layers, and find application in actuators, energy storage, flexible electronics, supercapacitors and catalysis [136–139]. To cater the functional requirements of this wide range of applications, a variety of fabricating techniques have been developed including self-assembly, template guided growth, organic sol-gel reactions and lightscribe patterning technology [140] which yield different morphologies, see Fig. 2.2. Though the mechanical properties of individual graphene layers are far superior to metals, but it remains to be a challenge to transfer these properties to the macroscopic level.

Self-assembly is often employed to construct 3D graphene architectures with hierarchical structures and novel functions based on the principles of colloid chemistry [139]. Also template-guided methods can produce 3D porous graphene networks with well-defined monolithic structures [141–145], see Fig. 2.2(a). In these methods graphene is deposited on a nickel template using chemical vapor decomposition (CVD) with methanol or ethanol as carbon source [141, 146]. The graphene foams thus obtained have excellent ligament interconnectivity providing a continuous path to inject charge. The ligaments consist of one or multiple graphene layers and have wrinkles on the surface which arise due to the different thermal expansion coefficients of Ni and graphene [147]. The wrinkles are proposed to improve the mechanical interlocking with polymer chains, resulting in a better adhesion when a graphene foam is integrated with a polymer to form composite materials [141]. The graphene foams serve as a template for the construction of high capacitance graphene/metal oxide composites which find application in supercapacitors. The free standing graphene

foams obtained with this method are extremely light and flexible with ultra low densities of $\approx$ 5 mg/cm^3, comparable to that of the lightest aerogel ($\approx$ 23 mg/cm^3). These graphene foams have a porosity as high as 99.7% and a specific surface area $\approx$ 850 m^2/g. The porosity of the graphene foam can be tailored by changing the methanol/ethanol concentration.

The 3D graphene network prepared by Biener et al. [30] consists of curved and intertwined monolayer graphene, see Fig. 1.1(a). These have a density of $\approx$ 200 mg/cm^3 and surface area of 3000 m^2/g with submicron pore sizes. There are 3D porous structures [148] with many single graphene layers intertwined throughout the structure as in samples of [30], but architecturally they are different, see Figs. 1.1(a) and 2.2(b). These foams consist of wrinkled single layer graphene sheets with dimensions of a few nanometers (4-6 nm), with at least some covalent bonds between each other. They have ultrahigh surface areas (3523 m^2/g) with pore sizes mainly in the range 1-10 nm. Graphene nanofoams produced by an ion-exchange method [149] are disordered and have pores ranging from 2 to 5 nm, see Fig. 2.2(c). Another method to produce disordered nanofoams is by depositing graphene sheets on silica spheres [150]. The nanofoams thus obtained have a specific area of 851 m^2/g and pore sizes ranging from 30 to 120 nm, see Fig. 2.2(d). Lee et al. [151] fabricated porous three dimensional graphene films on a SiO2/Si substrate with an average pore size of approximately 40-50 nm. Xiao et al. [152] used a lithographic technique to prepare ordered nanofoams having hollow ligaments with multilayered walls and pore sizes of 500 nm, see Fig. 2.2(e). Qiu et al. [99] prepared graphene hexagonal honeycomb lattices, see Fig. 2.2(f), using a freeze casting technique.

2.2 Mechanical properties

2.2.1 Metal nanofoams

By miniaturizing the dimensions of porous metals, two physical mechanisms become important: size-dependent plastic strength and surface stress.

The strength of a metal is determined by its ability to resist plastic deformation. It is classically seen as a material property, intrinsically linked to the material itself and therefore independent of the material's dimensions. However, since the early '90s it has become convincingly clear that the plastic strength is size dependent at the scale of tens of microns and smaller. This has been experimentally shown for specimens under torsion [153, 154], bending [155, 156] and indentation [157–159], resulting in an increasing strength with decreasing dimensions, which is commonly addressed as "smaller is stronger". The fact that

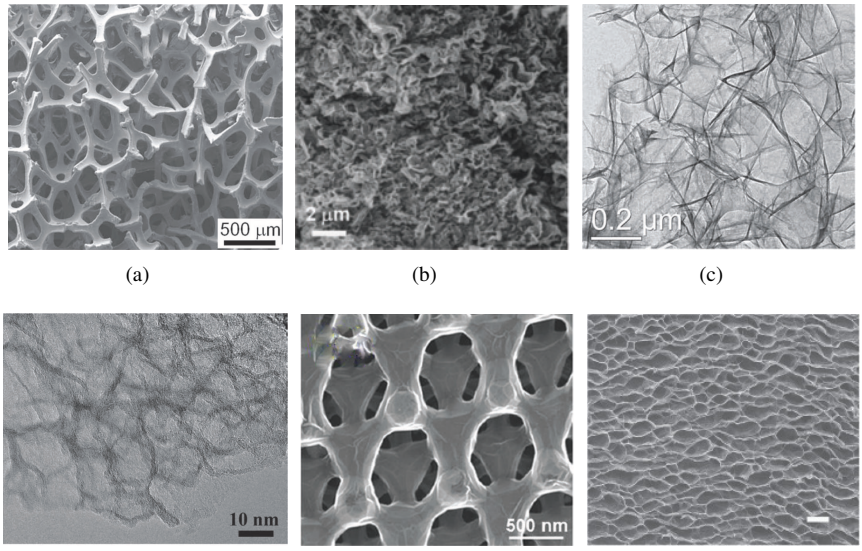


Figure 2.2: Different morphologies of graphene nanofoams. (a) Graphene foams prepared by using nickel foam as a template [146]. (b) Graphene foam prepared by hydrothermal carbonization of a mixture of carbon sources with graphene oxide [148]. (c) Graphene nanofoam prepared by an ion-exchange method [149]. (d) Graphene foam prepared by depositing graphene sheets on silica spherical templates [150]. (e) Graphene foams prepared from pyrolyzed photoresist films using lithography [152]. (f) Graphene hexagonal honeycombs fabricated by freeze casting of a partially reduced graphene oxide (the scale bar is 50 μm) [99].

the strength of metals increases with decreasing size, in bending as well as in stretching, opens opportunities for cellular metals. Although size effects lead to new material properties [26, 76, 160, 161], the combination of architecture and characteristic lengths also play a crucial role [1, 26, 76, 90, 124, 162–166]. For example, nanofoams with a well connected network of ligaments and size dependent ligament strength have seemingly conflicting properties: high strength and low specific weight. The stiffness, yield strength, and ultimate strength of conventional, macroscopic foams, with characteristic microstructural sizes on the order of micrometers and more, can be predicted by the well established Gibson and Ashby scaling relations in terms of the relative density of foams [167]. However, recent experimental studies on submicron Au columns [131, 168–171] and nanowires [172], which closely resemble the ligaments in gold nanofoams, show that the strength increases with de-

creasing ligament size. This compels one to modify the existing scaling relations to account for the size effect.

The yield strength of NPG has been experimentally measured by various methods including microtension, nanoindentation, and buckling-based metrology [162, 163]. It was found that the mechanical properties of NPG depend sensitively on microstructural parameters such as the ligament size and relative density. For example, the yield strength has been found to increase from 33 to 171 MPa as the ligament diameter decreases from 50 to 10 nm [162]. In case of macroscopic foams the yield strength is given by [167]

$$\sigma^*_{\mathrm{pl}}/\sigma_{\mathrm{y}} = C_{\mathrm{y}}\rho^{*3/2}, \tag{2.1}$$

where σ^*_{pl} is the yield strength of the foam, σ_{y} is the yield strength of the solid material, $C_{\mathrm{y}} = 0.3$ and ρ^* is the relative density of the foam. In case of NPG, the ligament strength values can be back calculated from the scaling relation in Eq. (2.1), yielding 880 MPa to 4.6 GPa as the ligament diameter decreases from 50 to 10 nm. These values are 10-100 times higher than that predicted from the Gibson-Ashby model [122, 131], and are consistent with recent uniaxial compression tests on submicron sized Au columns [131, 170, 171]. In [131] the yield strength of the Au columns is shown to follow the power law d^n, with d being the column diameter and $n = -0.6$. Another empirical relation (Hall-Petch) is presented by Hodge et al. [124] based on mechanical tests performed on NPG samples with ligament sizes in the range 10-900 nm where the yield strength of the ligament scales with $d^{-1/2}$:

$$\sigma_{\mathrm{y}} = \sigma_{\mathrm{ys}} + k_{\mathrm{Au}}d^{-1/2}, \tag{2.2}$$

where $\sigma_{\mathrm{ys}} = 200$ MPa is the size-independent yield stress of gold and $k_{\mathrm{Au}} = 9821$ MPa $\mathrm{nm}^{1/2}$. Viswanath et al. [173] performed mechanical tests on NPG samples with diameters ranging from 5 to 150 nm and presented a similar scaling relation, but with the yield strength scaling with $d^{-0.3}$. Cheng et al. [166] have performed an extensive study on the strength of gold, silver, copper and palladium nanofoams. They found that the yield strength of ligaments can be well compared with the plastic collapse model presented in Eq. 2.2 [124].

Mathur et al. [163] carried out a detailed study on the size effects on the Young's modulus of NPG. They performed mechanical tests on 100 nm thick NPG samples of ligament diameters ranging from 3 to 40 nm. While the Young's modulus lies between 6 and 12 GPa for samples with ligament diameters greater than 12 nm [122, 131, 174], for samples with ligament diameters less than 12 nm it increases with decreasing ligament size, reaching a maximum of 40 GPa for a ligament size of 3 nm. There are a couple of theo-

retical studies [175, 176] in which the effect of surface stresses on the Young's modulus of cellular materials at smaller length scales has been studied. However, the size effect predicted by these models is pronounced only up to a ligament size of 4 nm. Mechanical tests [122, 126, 131, 162, 163, 174, 177, 178] that have been carried out on NPG samples with ligament diameters in the range 20-70 nm show no size effect on the Young's modulus. However, the Young's modulus of these samples are found to be higher than the values obtained by the existing scaling relations with relative density. Liu and Antoniou [112] proposed that mass agglomeration at the junction leads to the enhanced modulus. These geometrical effects are taken into account by a new scaling relation for the Young's modulus which is expressed in terms of ligament thickness, ligament length and junction size.

While gold is a ductile material, NPG exhibits brittle failure [120, 122, 179, 180] and is currently not suitable for applications involving mechanical loading or solid contact. Interestingly, individual ligaments deform in a ductile way, with significant necking, as expected for Au [122]. Li and Sieradzki attributed this to a ligament size dependent ductile-brittle transition [120].

Molecular dynamics studies have been carried out to explore the stiffness, strength and stability of NPG [181, 182]. Mechanical tests are performed on virtual samples generated by phase field modeling having morphologies that closely resemble those of NPG obtained by dealloying. Farkas et al. [181] studied the compression/tension asymmetry of the yield strength. Sun et al. [182] studied the strength of NPG by performing tensile tests on NPG samples with ligament diameters in the range 2.45-4.08 nm and relative densities in the range 0.24-0.36. While no size effects are observed on the Young's modulus and yield strength, the ultimate strength is found to scale with a -0.44 power of the ligament diameter. The tensile strain leads to progressive necking and rupture of some ligaments, ultimately resulting in failure of the material.

2.2.2 Graphene nanofoams

The major challenge in fabricating graphene nanofoams lies in carrying the exceptional properties of two-dimensional graphene over to the three-dimensional nanofoam. Engineering applications of these materials demand a long lifetime which depends on their mechanical properties. So far, electrical and catalytic properties of graphene nanofoams have been explored extensively, while only a few groups explored their mechanical properties. The disordered graphene nanofoams of Biener et al. [30], with a relative density of ≈ 0.1, are found to have a modulus of 300-1000 MPa, Meyer hardness of 20-100 MPa and weight-bearing

capacity of 200 kg/cm^3.

Qiu et al [99] fabricated hexagonal graphene honeycomb structures with densities ranging from 0.56 to 6.6 mg/cm^3 having architectures that become more disordered with decreasing density. The tightly packed cell walls consist of graphene layers stacked on top of each other over a thickness of 10 nm. Like a typical bending dominated structure, the compression modulus scales with the square of the density of the honeycomb, with a modulus of around 0.03 MPa for the more ordered structures of relative density 0.004. The samples of 5.1 mg/cm^3 density were found to have an excellent resilience in compression. The samples were found to buckle when loaded in compressed and regain their shape when unloaded, even when subjected to 80% strain. On the other hand, the more disordered samples of 0.56 mg/cm^3 density were found to collapse under compression. The energy loss coefficient of these materials ranges between 67 and 87% depending on the density. The high energy loss coefficient was reported to be due to the interlayer van der Waals adhesion and friction during bending and buckling.